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# ITO nanowire networks coating on $\mu$ -hole arrayed substrate as superbroadband antireflection layer



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#### ABSTRACT

We have fabricated the  $\mu$ -hole array on silicon surface using short-pulse laser, and prepared ITO-nanowire networks via polystyrene spheres. They formed a super-broadband antireflection layer that has gradual refractive index and excellent antireflective properties. The reflectance reached about 15% in the band of 400–2500 nm, and the surface could maintain a strong electrical conductivity. The finite difference time domain method was used to analysis the effect of  $\mu$ -hole array on the light field, and the antireflection effect of ITO nanowires was calculated. To make use of the light energy in infrared band more effectively, it is a key role to keep a certain hole-spacing. This method will provide a novel and practical model for surface texturing to improve the efficiency of solar cells by using the infrared band light.

## 1. Introduction

With the development of solar cell industry, enhancing the efficiency of solar cells has been of great interest in recent years. The cell surface must be highly antireflective for the broadband solar spectrum over a wide angular range such that the solar energy can be sufficiently absorbed and trapped in the cell. Therefore, the antireflection (AR) coating has been widely studied and applied (Brückner et al., 2013; Bouffarn et al., 2008; Shimomura et al., 2010; Ye et al., 2015; Phillips et al., 2011). A single layer with a quarter-wavelength thick was used as conventional AR coating. But, it is well known that such single layer AR coating does not operate well over a broad range of wavelengths (Bloemer et al., 2007). In theory, this deficiency can be overcome by fabricating AR coatings in which the refractive index (RI) is graduated from the low RI-material to the high one (Kennedy and Brett, 2003; Rahman et al., 2015; Conrad et al., 2016; Yang et al., 2016). A graded effective medium could be served to reduce index mismatch at the interface and eliminate reflection. However, the fabrication process of multilayer with graduated RI is more complex and the material is difficult to choose (Kanamori et al., 1999; Matsumura et al., 2016; Saylan et al., 2015). At present, the surface texturing is the most common method to reduce the reflectivity, which is always prepared as micro/

nano array structure by dry or wet etching (Fan et al., 2013; Tan et al., 2012; Ha et al., 2014; Ye et al., 2016). This method greatly reduced the reflectivity of light in the visible band, but the decreasing effect in a wider band (Shen et al., 2016), especially in the infrared band, was not obvious. Finding an effective way to control the surface micro- or nano-structure array for improving the effect of AR in super-broadband, it is one of the urgent problems. Nowadays, short-pulse laser-solid interaction is frequently used for non-contact, chemical-free material processing (Wang et al., 2016). Laser micro-fabrication technology could be used to control the micro-structure array on the Si surface efficiently and rapidly (Deng and Ki, 2016; Fan et al., 2015). Micro structured surface with graded-index and excellent AR properties has been fabricated to reduce the reflection from air-material interface, which is developed by using laser interference lithography.

The plant foliage has optimized structure to absorb the solar energy after millions of years of natural evolution (Huang et al., 2016). Based on studying the surface morphology of leaves (Yong et al., 2017), a bionic structure was proposed in this paper. The indium-tin oxide (ITO) nanowires were prepared on micro-hole arrayed substrate with certain spacing. In this structure, the micro-hole array that was used to control the distribution of light intensity with different wavelengths was prepared by short-pulse laser patterning on the Si surface. And then, the

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**Fig. 1.** The schematic diagram of fabrication process: (a) the 355 nm laser was focused on the wafer surface; (b) cross-section of  $\mu$ -hole array, the hole shows a conical shape; (c) the PS spheres were coated on the  $\mu$ -hole arrayed silicon surface; (d) ITO nanowires were fabricated by E-beam deposition.

ITO nanowires were fabricated on the micro-hole arrayed surface via polystyrene (PS) spheres (Li et al., 2016), which could be used to limit the scatting and the reflection of light. We have combined ITO nanowires and micro-holes to form an excellent super-broadband antire-flection layer.

Firstly, we will present the preparation method and process of micro-holes and ITO nanowires. And then, the effect of micro-hole array on the light field is simulated by the finite difference time domain (FDTD) method. Finally, the different micro-hole arrays with same ITO-nanowire coating are fabricated, and the AR effect is researched.

## 2. Experimental process

Fig. 1 is the schematic diagram of fabrication process. Fig. 1a shows that the short-pulse laser beam was focused on the surface of cleaned silicon. The silicon surface can be etched by an ultrahigh energy laser pulse in very short time. The cone-hole array was formed on the silicon surface after the laser scanning by repeating the ablation process. The spacing of micro-holes was controlled by the moving speed of platform and laser pulse repetition rate. The Q-switched nanosecond laser  $(\lambda = 355 \text{ nm}, \text{ pulse duration: } 40 \text{ ns}, \text{ pulse repetition rate: } 1 \text{ KHz}, \text{ power:}$ 0.08 W) was used to etch the sample in a fast scanning mode. Fig. 1b is the morphology of etching result, and the cone-hole size is about 10 µm in diameter. And then, the polystyrene spheres (PS, 500 nm in dia.) were coated on the µ-hole arrayed silicon surface by self-assembly, shown in Fig. 1c. Lastly, the ITO-nanowire (ITO-NW) networks were fabricated by electron beam evaporation (deposition rate: 0.1 nm/s, chamber temperature: 300 °C, pressure  $< 5 \times 10^{-4}$  Pa, time: 1800-2000 s). All the holes and the whole surface were covered by ITO-NW networks Fig. 1d).

Three samples with different hole-spacing were designed. The spacing is  $15 \,\mu\text{m}$  (sample-1),  $30 \,\mu\text{m}$  (sample-2), and  $50 \,\mu\text{m}$  (sample-3), respectively. And a special sample was also prepared, on which the hole-spacing is equal to the hole-diameter. The morphology of the fabricated  $\mu$ -hole array pattern was characterized by a scanning electron microscopy (SEM). The reflectance of all samples was measured by the ultraviolet spectrophotometer (Lambda 750 s). In the test process, the integrating sphere with a diameter of 100 mm was used, and in which two detectors were built. One detector is photomultiplier tube (PMT), which is designed for UV/Vis range. The other one is lead sulfide (PbS) detector, which is used for near infrared/mid infrared light. The detectors are switched automatically at the wavelength of 860.8 nm. The FDTD was used to calculate the modulation effect of light field with  $\mu$ -hole array.



**Fig. 2.** (a) Obvious diffraction fringes appearing on the surface of silicon with  $\mu$ -hole array. The SEM image of (b) patterned area, (c) a single hole; (d) the cross-section for one hole.

#### 3. Results and discussion

### 3.1. Morphology of µ-hole array with ITO-NW networks

Fig. 2a shows the reflection phenomenon of sunlight on patterned and unpatterned Si surfaces. Due to the influence of  $\mu$ -hole array, the reflection of light in the patterned region shows the diffraction fringes. Fig. 2b is the top view of the patterned region. Fig. 2c is the SEM image for one hole, and the hole diameter is about 10 µm. Fig. 2d is the crosssection view for a single hole, and the hole depth is 14 µm, showing a conical shape.

The ITO-NW networks were obtained by e-beam depositing for 2000 s via PS sphere with diameter of 500 nm. The patterned Si surface from the result of Fig. 2 was covered by ITO nanowires. Fig. 3a is the surface morphology of the sample with ITO-NW networks on the  $\mu$ -hole arrayed Si. Fig. 3b is the ITO-NW networks on the plane area and the nanowires are intertwined with each other as a network. The insert is the cross-section image, and the thickness of this layer is ~ 2  $\mu$ m. Fig. 3c



**Fig. 3.** (a) ITO-NW networks on the surface of  $\mu$ -hole array Si. (b) The ITO-NW networks on the plane area, insert is the cross-section image. (c) Single hole was covered by ITO-NW networks completely. (d) All the inner-wall of the hole was covered by ITO-NW networks. The insert is the large image of bottom area.

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